Tetrahedron Letters,Vol.29,No.15,pp 1797-1798,1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Press plc

NEW LIQUID CRYSTALS HAVING 4,4'-BIPHENANTHRYL CORE

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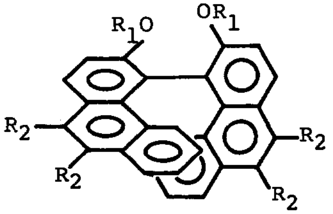
4,4'-Biphenanthryl carrying six or four long tails forms a stable thermotropic liquid crystalline mesophase, giving promises of preparing new mesogens having skewed-disc shaped core

The control of liquid crystalline molecular allignment including discotic mesophase is actively investigated for elaboration of molecular materials.[1,2] Of particular interest is chiral mesogens such as cholesteric or chiral smectic type,[3,4] from the viewpoint of electric stimulus response. In the course of investigation of new functional liquid crystals,[5-7] we found that 4,4'-biphenanthryl derivatives, 1a and 1b, which carry six and four long tails, respectively, form stable liquid crystalline mesophase. This may open a way to a new class of chiral liquid crystals other than cholesteric or chiral smectic type.

Treatment of (±)-3,3'-dihydroxy-4,4'-biphenanthryl (2)[8] with dodecyl bromide or methyl iodide in the presence of ^{t}BuOK in THF gave 3,3'-bis(dodecyloxy)-4,4'-biphenanthryl (3a) or 3,3'-bis(methoxy)-4,4'-biphenanthryl (3b), respectively.[9] The oxidation of 3 to the corresponding bis-o-quinone (4a, 4b) was successfully carried out by using CrO_3 in AcOH.[10] The bis-o-quinone (4a, 4b) was reduced readily with $Na_2S_2O_4$ affording 3,3'-bis(alkoxy)-9,9',-10,10'-tetrahydroxy-4,4'-biphenanthryl (5a, 5b). Compound 5 was readily re-oxidized by air to 4 and, therefore, 5 was without isolation condensed with octanoic acid or dodecanoic acid by using DCC in THF to give the desired compound, 1a or 1b, respectively.[11] The preparation route is



(±)-1 a $R_1 = -C_{12}H_{25}$ $R_2 = -OCOC_7H_{15}$
b $R_1 = -CH_3$ $R_2 = -OCOC_{11}H_{23}$

(The structure of (+)-isomer is pictured for simplicity)

	R_1	R_2
2	-H	-H
3a	$-C_{12}H_{25}$	-H
b	$-CH_3$	-H
4a,b	do	=O
5a,b	do	-OH

Scheme I

$$2 \xrightarrow[\substack{R_1X\ (X=Br,\\ I)\\ {}^tBuOK/THF}]{} \begin{matrix}3a(95\%)\\ 3b\end{matrix} \xrightarrow[\substack{CrO_3/\\ AcOH}]{} \begin{matrix}4a(37\%)\\ 4b\end{matrix} \xrightarrow[\substack{aq.\\ Na_2S_2O_4}]{} \begin{matrix}(5a)\\ (5b)\end{matrix} \xrightarrow[\substack{C_7H_{15}CO_2H\ or\\ C_{11}H_{23}CO_2H\\ DCC/THF}]{} \begin{matrix}1a(41\%)\\ 1b\end{matrix}$$

summarized in Scheme I.

Below ca. 43°C, 1a was solid but a thermotropic mesophase appeared above 43°C, judging from differential scanning calorimetric and polarized microscopic observations. Similarly, 1b took a mesomorphic state above ca. 113°C. Their birefringent textures under the polarizing microscope remained stable up to 180 - 200°C and the transition to the isotropic phase was not observed. In DSC, neither 1a nor 1b showed any appreciable endothermic peak above 180°C in agreement with the microscopic observation (a slight brown coloration began at 180°C for 1a or at 200°C for 1b though, suggesting thermal decomposition). In conclusion, 1a and 1b are new thermotropic liquid crystalline compounds, giving promises of preparing new, chiral biphenanthryl-based mesogens with a "skewed"-disc core, since it is known that (±)-4,4'-biphenanthryl can be resolved into chiral isomers which are very sluggish to racemization as reported.[8]

Aknowledgment K.Y. thanks for the financial support of Japan Ministry of Education, Science, and Culture.

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9 3a: MS m/e(rel. int.) 722(M, 100), 554(13), 386(41); NMR($CDCl_3$) δ 0.7-1.7 (46H), 3.1-3.8(4H, $-OCH_2-$), 6.6-8.2(14H, aromatic); IR(neat) 1260 cm^{-1}. 3b: NMR($CDCl_3$) δ 3.4(s, 6H, -OMe), 6.5-8.1(14H, aromatic).

10 4a: MS m/e(rel. int.) 782(M, 100), 754(54), 390(83); NMR($CDCl_3$) δ 0.7-1.7 (46H), 3.5-4.0(4H, $-OCH_2-$), 6.9-8.3(12H, aromatic); IR(neat) 1660, 1260 cm^{-1}. 4b: NMR($CDCl_3$) δ 3.6(s, 6H, -OMe), 6.9-8.3(12H, aromatic).

11 1a: FD-MS m/e 1290(M); NMR($CDCl_3$) δ 0.7-2.1(98H), 2.6-2.9(8H, $-COCH_2-$), 3.3-3.8(4H, $-OCH_2-$), 6.8,6.9,7.0(2H, $H_{6,6'}$), 7.2-7.3(2H, $H_{2,2'}$), 7.3-7.4 (2H, $H_{7,7'}$), 7.7,7.8(2H, $H_{8,8'}$), 7.9,8.0(2H, $H_{1,1'}$), 8.3,8.4(2H, $H_{5,5'}$); IR(neat) 1760, 1110 cm^{-1}. 1b: NMR($CDCl_3$) δ 0.7-2.1(84H), 2.6-2.9(8H, $-COCH_2-$), 3.4(s, 6H, -OMe), 6.8-7.1(2H, $H_{6,6'}$), 7.3-7.4(4H, $H_{2,2',7,7'}$), 7.7,7.8(2H, $H_{8,8'}$), 8.0,8.1(4H, $H_{1,1',5,5'}$)

(Received in Japan 6 January 1988; accepted 4 February 1988)